Raman spectroscopic study of the antimonate mineral brandholzite $Mg[Sb(OH)_6]\cdot 6H_2O$

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Raman spectra of brandholzite $Mg[Sb(OH)_6]\cdot 6H_2O$ were studied, complemented with infrared spectra, and related to the structure of the mineral. An intense Raman sharp band at 618 cm^{-1} is attributed to the SbO symmetric stretching mode. The low intensity band at 730 cm^{-1} is ascribed to the SbO antisymmetric stretching vibration. Low intensity Raman bands were found at 503, 526 and 578 cm^{-1}. Corresponding infrared bands were observed at 527, 600, 637, 693, 741 and 788 cm^{-1}. Four Raman bands observed at 1043, 1092, 1160 and 1189 cm^{-1} and eight infrared bands at 963, 1027, 1055, 1075, 1108, 1128, 1156 and 1196 cm^{-1} are assigned to δ SbOH deformation modes. A complex pattern resulting from the overlapping band of the water and hydroxyl units is observed. Raman bands are observed at 3240, 3383, 3466, 3483 and 3552 cm^{-1}, infrared bands at 3248, 3434 and 3565 cm^{-1}. The first two Raman bands and the first infrared band are assigned to water stretching vibrations. The two higher wavenumber Raman bands observed at 3466 and 3552 cm^{-1} and two infrared bands at 3434 and 3565 cm^{-1} are assigned to the stretching vibrations of the hydroxyl units. Observed Raman and infrared bands are connected with O-H…O hydrogen bonds and their lengths 2.72, 2.79, 2.86, 2.88 and 3.0 Å (Raman) and 2.73, 2.83 and 3.07 Å (infrared).

Keywords: brandholzite, antimonate, antimonite, molecular water, Raman, infrared, spectroscopy

Introduction

The mineral brandholzite, trigonal $MgSb_2(OH)_{12}\cdot 6H_2O$, was originally described as plate-like crystals up to 1 mm in size in association with stibnite from mining district Brandholz-Goldkronach (Bavaria, Germany) [1]. Later, it was also

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found as tiny colorless aggregates at the Krížnica mine, the Pernek deposit, the Malé Karpaty Mountains, western Slovakia, Slovak Republic [2,3] in association with stibnite, sulphur, aragonite, gypsum and antimony-ochres. The structure of the mineral has been published [1,4]. Its crystal structure is isotypic with bottinoite [5,6]. The mineral is isotypic with synthetic $Co(H_2O)_6[Sb(OH)_6]_2$ [4] and bottinoite, $Ni(H_2O)_6[Sb(OH)_6]_2$ [5-7].

Farmer reported the infrared spectra of some synthetic antimonite minerals (see page 413 and 414 with Tables 17. XVIII and XIX) [8]. For the synthetic compound $NaSb(OH)_6$ which is a compound with an octahedral structure, infrared bands were observed at 600 and 628 cm^{-1} (very intense), 735, 775 cm^{-1} (medium intensity), and 528 and 586 cm^{-1}. Siebert researched the infrared spectra of selected synthetic antimonates [9,10]. Siebert assigned bands in the 528 to 775 cm^{-1} region to the stretching vibrations of SbO units; in the 1030 to 1120 cm^{-1} to the deformation modes of SbOH units and in the 3220 to 3400 cm^{-1} to the stretching bands of SbOH and water units.

It is interesting to note that only very few papers have been published on the spectroscopy of antimonate minerals. What research has been published is related to the analysis of pigments [11-13]. Some spectroscopic studies of calcium and lead antimonates have been forthcoming [14-16]. Very few studies of related minerals such as mineral antimonates have not been undertaken [17-19]. It was found that the hydroxyl unit was coordinated directly to the metal ion and formed hydrogen bonds to the arsenate anion [20]. Raman spectroscopy has proven especially useful for the study of related minerals [21-29]. As part of a comprehensive study of the molecular structure of secondary minerals containing oxy-anions [30-40], formed in the oxide zone, using IR and Raman spectroscopy, we report the Raman properties of the antimonate mineral brandholzite. The spectra are related to the mineral structure.

Experimental

Mineral

The studied sample of the mineral brandholzite was found at Krížnica mine, the Pernek deposit, the Malé Karpaty Mountains, western Slovakia, Slovak Republic [39], and is deposited in the mineralogical collections of the National Museum Prague. The sample was analysed for phase purity by X-ray powder diffraction. No minor significant impurities were found. Its refined unit-cell parameters for trigonal space group *P*3, *a* 16.1076(9), *c* 9.8628(9) Å, *V* 2216.1(2) $Å^3$, are comparable with the data published for this mineral phase [1]. The mineral was analysed by electron microprobe (Cameca SX100, WD mode) for chemical composition. The results (mean of 2 point analyses, recalculation to 100 wt. %) are MgO 6.11, CaO 0.52, FeO 0.16, Sb_2O_5 55.91, H_2O 37.30 wt. %, sum 100.00 wt. %. The water content was calculated on the basis of theoretical content (OH) = 12 and H_2O = 6 *pfu*. The resulting empirical formula is $(Mg_{0.88}Ca_{0.06}Fe_{0.01})_{\Sigma 0.95}(H_2O)_{6.00}[Sb(OH)_6]_{\Sigma 2.01}$.

Raman spectroscopy

The crystals of brandholzite were placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a

Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Further details have been published [21-29].

IR spectroscopy

The FTIR spectrum of brandholzite was obtained with the FTIR Nicolet 740 spectrometer using the conventional KBr-disk technique. Infrared spectrum in the range 4000-400 cm^{-1} was obtained by the co-addition of 32 scans with a resolution of 2 cm^{-1} and a mirror velocity of 0.1496 cm/s. Spectral manipulation such as baseline adjustment, smoothing and normalization were performed using the OMNIC software package (Thermo Electron Corporation). Band component analysis was undertaken using the same software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed of varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process which was undertaken until reproducible results were obtained with minimum value of standard errors (usually lower than 2, the range for brandholzite spectra is 1.30-0.20).

Results and discussion

Raman spectroscopy

The Raman spectrum of brandholzite in the 400 to 800 cm^{-1} region is shown in Fig. 1. The spectrum shows some complexity with a number of overlapping bands observed at 618, 630 and 730 cm^{-1} with additional low intensity bands found at 503, 526 and 578 cm^{-1}. Infrared bands were observed at 527, 600, 637, 693, 741 and 788 cm^{-1} (Supplementary Figure 1S). According to Siebert [9,10] all bands in these positions are assignable to stretching vibrations. The observation of multiple bands in the Raman spectrum provides evidence for the non-equivalence of SbO units in the brandholzite structure. In the infrared spectrum of antimony pentoxide an intense band is observed at 740 cm^{-1} and low intensity bands at ~370, 450 and 680 cm^{-1} [41]. The infrared spectrum of valentinite $(Sb_2O_3)_4$ showed bands in similar positions [41]. Farmer reported the band positions of synthetic antimonates of formula $MSbO_4$ where M is Cr, Fe, Ga or Rh with a rutile type structure [8]. As such these structures should have four Raman active bands ($A_{1g} + B_{1g} + B_{2g} + E_g$) and four infrared active bands ($A_{2u} + 3E_u$). Infrared bands were observed in the 660 to 735 cm^{-1}, 520 to 585 cm^{-1}, 285 to 375 cm^{-1} and 170 to 190 cm^{-1}. Although no assignment was given to these bands but one possible interpretation is that the first band is attributed to the antisymmetric stretching mode, the second to the symmetric stretching mode, the third to bending modes and the fourth to a lattice modes. Hence the bands of brandholzite at around 618 cm^{-1} are attributable the symmetric stretching modes. The observation of several bands in this region suggests that the $Sb(OH)_6^{2-}$ are not equivalent. In the infrared spectrum of the compound $NaSb(OH)_6$ which has an octahedral structure, a very intense band is observed at 628 cm^{-1} with bands of lower intensity at 775 and 528 cm^{-1} [8].

The Raman spectrum of brandholzite in the 100 to 400 cm^{-1} region is displayed in Figure 2. Intense Raman bands are observed at 303, 318 and 340 cm^{-1}. One likely assignment of these bands is to OSbO bending modes. Such an assessment fits well with the assignment of bands for $MSbO_4$ structures as reported by Farmer [8]. The observation of multiple bands suggests the non-equivalence of SbO units in the

brandholzite structure. Other low intensity bands are observed at 115, 147, 191, 232 and 252 cm^{-1}. Low wavenumber bands are observed for $MSbO_4$ [8].

Raman bands in the 900 to 1800 cm^{-1} region are reported in Fig. 3. Raman bands in this spectral region are of a very low intensity. (The scaling factor is x7000 in Fig. 3) Two sets of bands are observed (a) in the 1000 to 1200 cm^{-1} region and (b) centred upon 1648 cm^{-1}. Four Raman bands are observed at 1043, 1092, 1160 and 1189 cm^{-1}. Eight infrared bands at 963, 1027, 1055, 1075, 1108, 1128, 1156 and 1196 cm^{-1} were observed (Supplementary information Figure 2S). These bands are assigned to δ SbOH deformation modes. Siebert reported four infrared bands at 1030, 1075, 1105 and 1120 cm^{-1} for the synthetic compound $NaSb(OH)_6$. The position and number of these infrared bands for his compound is in good agreement with the position of the Raman bands of brandholzite. The Raman band at 1648 cm^{-1} is ascribed to the water HOH bending mode. The position of the band for liquid water is ~1630 cm^{-1}. The position of the band at 1648 cm^{-1} and infrared bands at 1632 and 1653 cm^{-1} (Supplementary information Figure 3S) provides evidence for the water being strongly hydrogen-bonded in the brandholzite structure. Weak infrared bands at 1541, 1558 and 1739 cm^{-1} may be probably connected with overtones and/or combination bands.

The Raman spectrum of brandholzite in the 2600 to 3800 cm^{-1} region is shown in Figure 4. A complex pattern resulting from the overlapping bands of the water and OH units is observed. Raman bands are observed at 3240, 3383, 3466, 3483 and 3552 cm^{-1}, infrared bands at 3248, 3434 and 3565 cm^{-1}. The Raman bands at 3240 and 3383 cm^{-1} and the infrared band at 3248 cm^{-1} are assigned to water stretching vibrations. The higher wavenumber bands observed at 3466 and 3552 cm^{-1} (Raman) and 3434 and 3565 cm^{-1} (infrared) (Supplementary information Figure 4S) are assigned to the stretching vibrations of the OH units. There may be inferred a hydrogen-bonding network in the crystal structure of brandholzite with corresponding O-H…O hydrogen bond lengths [42] 2.72, 2.79, 2.86, 2.88 and 3.0 Å [Raman], and 2.73, 2.83 and 3.07 Å (infrared).

CONCLUSIONS

Raman spectra of brandholzite $Mg[Sb(OH)_6]\cdot 6H_2O$ have been studied and related to the structure of the mineral. Raman bands were assigned SbO stretching modes, δ SbOH deformation modes, OH stretching modes and water stretching and bending modes. O-H…O hydrogen bond lengths in the crystal structure of brandholzite were inferred from the Raman and infrared spectra.

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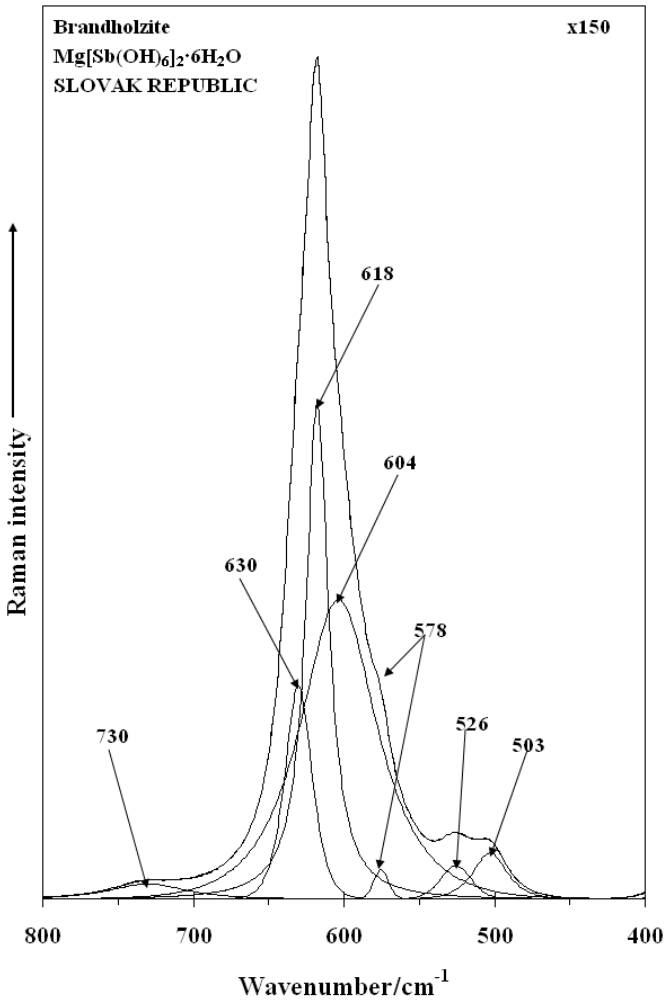
List of Figures



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299 **Figure 1**
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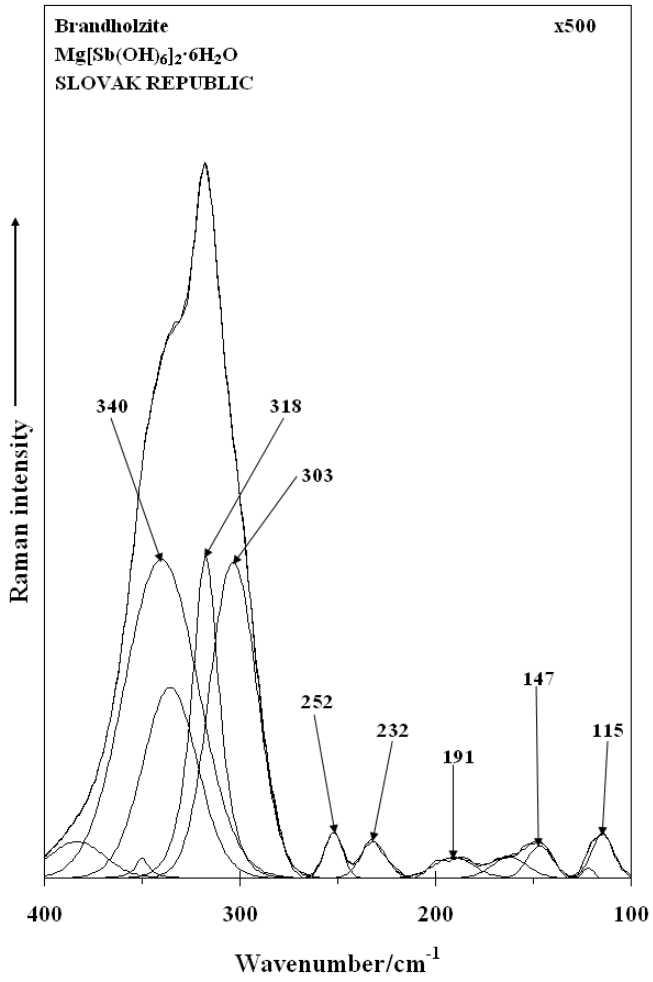
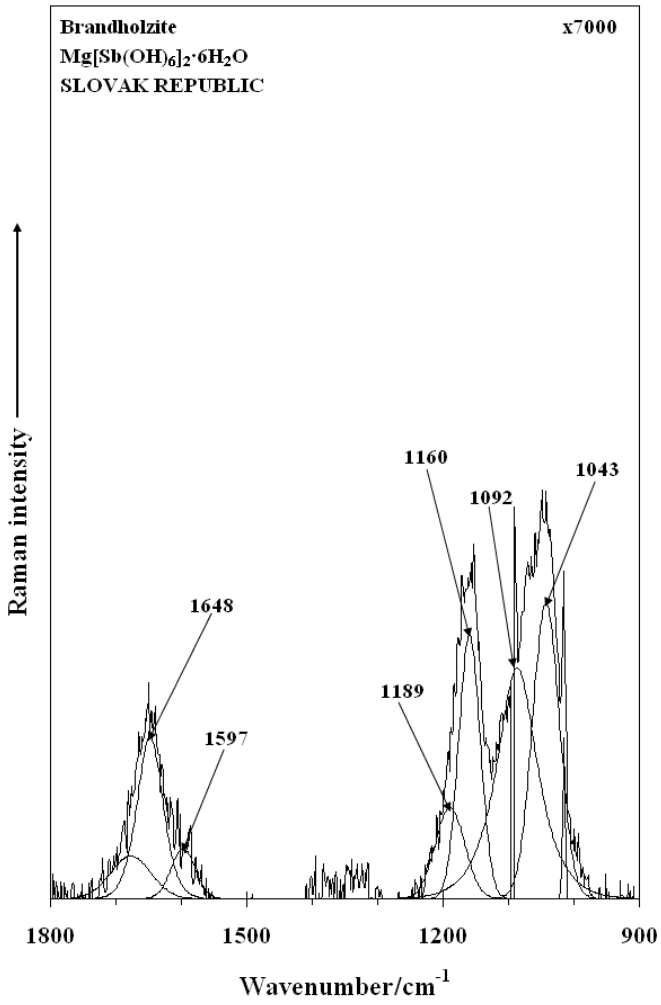

Brandholzite
x500
Mg[Sb(OH)6]2·6H2O
SLOVAK REPUBLIC
Raman intensity
340
318
303
252
232
191
147
115
400
300
200
100
Wavenumber/cm-1

Figure 2



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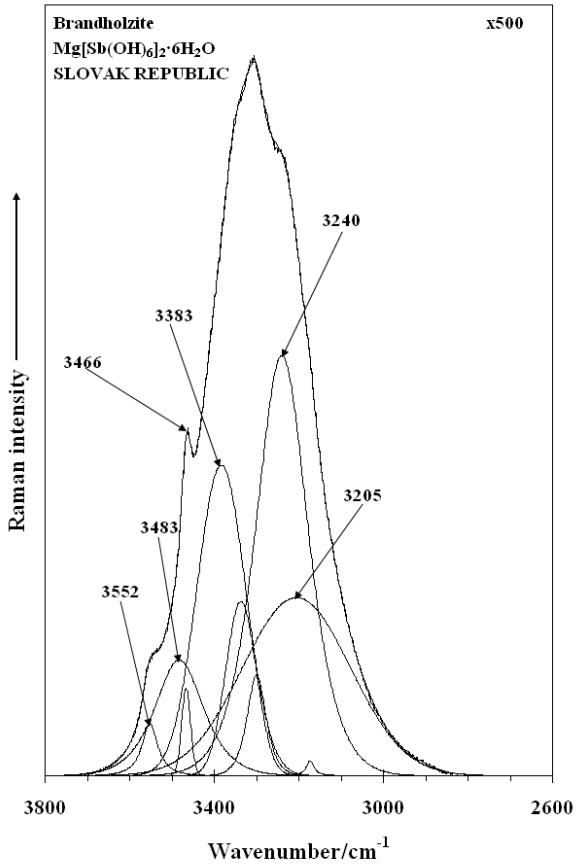

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314 **Figure 4**